Tselmovich V.A.,[1] Golovanova L.V.[2], Doronicheva E.V.[2], Doronichev V.B.[2], Kurazhkovskii A.Yu. [1] **Features of magnetic minerals from sedimentary rocks of Kuvinskaya cave (North-West Caucasus).** *UDC 550.3+902.1+902/904+551.8+551.21*

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Abstract. Sedimentary rocks of the Caucasus caves represent a unique natural archive of the region's geological history. These deposits contain important information about climate change, erosion and sedimentation processes, and the interaction of the biosphere and lithosphere. Magnetic minerals are a key tool for studying the origin and evolution of these rocks. The microstructure of approximately 1,000 particles from five layers (15 samples) of the Kuvinskaya Cave, collected by the Laboratory of Prehistory staff, was analyzed microscopically at the Borok Geophysical Institute of the Russian Academy of Sciences. The samples contained iron-containing (magnetic) particles—detrital and rounded—volcanic dust particles, hematite needles, as well as particles of background cosmic dust (BCD) or micrometeorites, some of which, with a nanoscale structure, can be attributed to cometary material (Tselmovich et al., 2025). A characteristic feature of the microparticles from the studied section were iron films covering almost all particles and the discovery of hematite needles.

***Keywords**: Caucasus; caves; Paleolithic; magnetic minerals; ferruginous films; volcanic dust; cosmic dust; climate; technogenic substance; optical and electron microscopy*

Introduction. Studies of magnetic particles found in caves in the Caucasus region are of significant interest for studying past climates and understanding the dynamics of natural processes. These studies help reconstruct climatic conditions of past eras, identify traces of volcanic eruptions, and analyze environmental changes. Magnetic minerals include ferromagnetic, antiferromagnetic, and paramagnetic materials. The most common of these are magnetite (Fe_3O_4), hematite (Fe_2O_3), and pyrrhotite (FeS). Paleomagnetism and petromagnetism are used to analyze the magnetic properties of sediments.

Subject and Methods of Study. The subject of the study was 15 samples collected in Kuvinskaya Cave (Golovanova et al., 2022). Kuvinskaya Cave is a multilayered Paleolithic (Middle Paleolithic-Epipaleolithic) settlement in the Otradnensky District of Krasnodar Krai. This is the only known stratified Paleolithic site with preserved cultural layers in the region. Location: The cave is located in the Kuva River valley (Kuban River basin), in a limestone scarp, at an altitude of 910 m above sea level and approximately 100 m above river level. The sedimentary rocks of the Caucasus caves represent a unique natural archive of the region's geological history. These deposits contain important information about climate change, erosion and sedimentation processes, and the interaction of the biosphere and lithosphere. Magnetic minerals are a key element in studying the origin and evolution of these rocks.

The main stages of the study include:

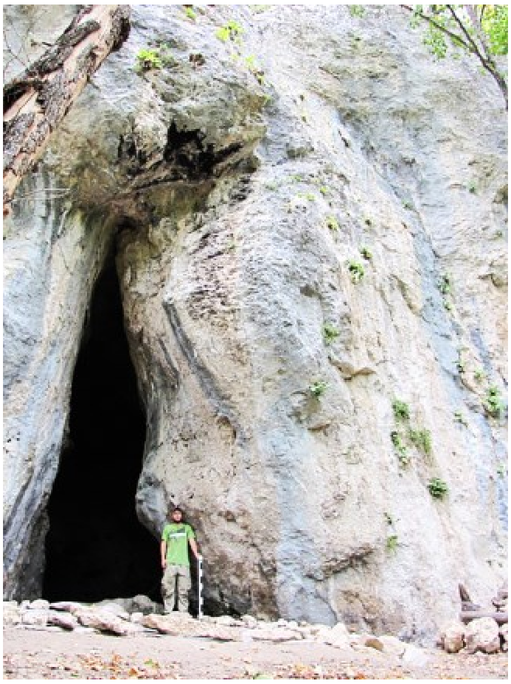
1. Sample collection: collecting sedimentary rock samples from a cross-section of the Kuvinskaya Cave.
2. Sample preparation: crushing and cleaning samples to remove foreign impurities.
3. Magnetic analysis: determining the intensity of magnetization along the depth of the section.
4. Microscopic study of magnetic particles using optical microscopy and scanning electron microscopy (SEM).
5. Interpretation of results: explanation of the nature of the discovered structures.

The study of magnetic particles discovered in caves of the Caucasus region is of significant interest for the study of past climates and understanding the dynamics of natural processes. These studies help reconstruct the climatic conditions of past eras, identify traces of volcanic eruptions, and analyze environmental changes.

An example of the successful application of magnetic mineralogy methods is the study of cave formations in the Greater Caucasus region and elsewhere. These studies reveal the presence of distinct layers with varying degrees of magnetization, which, along with other interdisciplinary analysis methods, indicates periodic changes in climate and sedimentation conditions (Pospelova et al., 2007; Djerrab et al., 2010).

Fifteen samples were analyzed at the Borok Geophysical Research Center of the Institute of Physics of the Earth, Russian Academy of Sciences. The samples were examined using an Olympus BX51M optical microscope and a Tescan Vega II scanning electron microscope.

During the study of the cave deposits, the remanent magnetization (Irs) of each layer was determined. High magnetization in samples 14 and 15 from layer 1 (Fig. 2) was confidently identified. This high magnetization was caused by a man-made factor: traces of foundry activity were recorded in the layer (Golovanova et al., 2022). Over 1,000 particles ranging in size from 0.5 μm to 200 μm were analyzed during the examination of dust particles removed from the surface of NdFeB magnets.



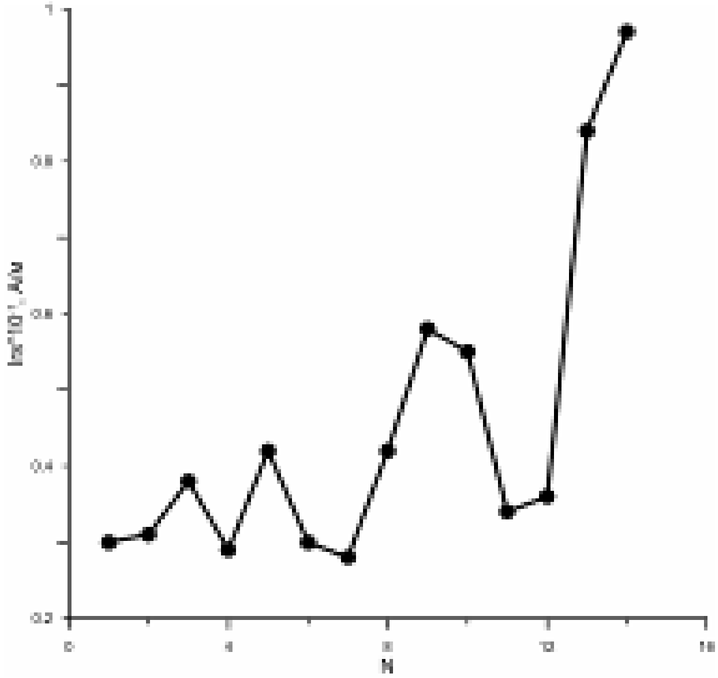


Fig. 1. Kuvinskaya Cave. View from the southeast along the axis of Kuvinskaya Cave.
Fig. 2. Residual magnetization (Irs) of layers (N, samples 1-15) /

Results. Discussion and Conclusions.

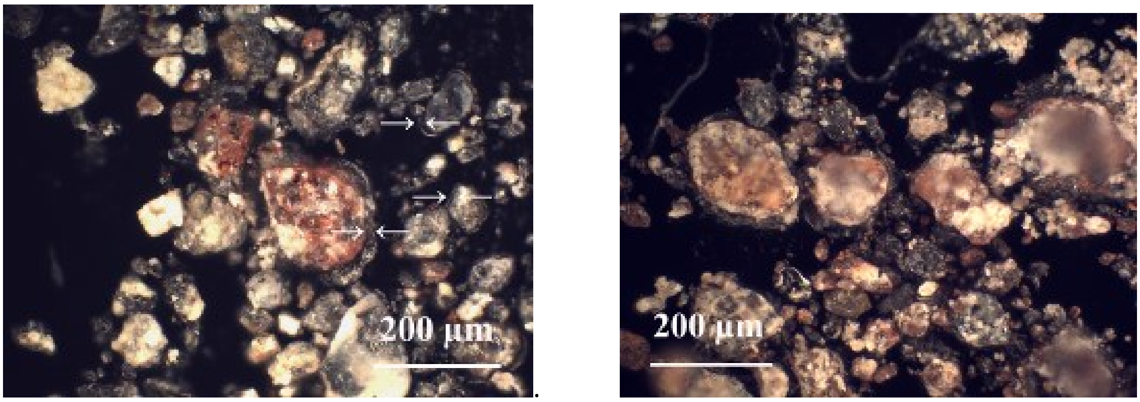
The following components of the collected dust were identified:

1. Particles with iron films (present everywhere, Fig. 3a, Fig. 3b).
2. Volcanic dust particles in layer 5, sample 2, Fig. 4a, Fig. 4b.
3. Background cosmic dust particles in sample #8, collected at the contact of layers 3 and 4, Figs. 5a, 5b.
4. Microsphere presumably of cometary origin, Fig. 5c.
5. Hematite needles, Fig. 6a.
6. Iron oxide particles of technogenic origin in layer 1 (traces of foundry production from the 10th-12th centuries AD), Fig. 6b.

The formation of iron films on sedimentary rock particles in Caucasus caves is associated with the activity of iron bacteria, which play a key role in the oxidation and accumulation of iron. Microorganisms actively participate in the transformation of iron through oxidation, fixation, and the release of iron-rich waste products. This creates the basis for the formation of thin layers of iron deposits that cover the surface of mineral particles and cave walls. The formation of iron films is determined by a complex of factors, among which microbiological processes are particularly significant. Microorganisms play a crucial role in iron oxidation, ensuring a steady supply of material for the formation of hard mantles characteristic of the mountainous regions of the Caucasus. The study of iron films in sedimentary rocks of Caucasus caves may indicate deposit formation conditions associated with a humid and hot climate. The discovery of unique hematite needle structures (Fig. 4b, group of small needles at top left, Fig. 6a) is of interest both for the study of geological processes and for understanding the microphysiology of organisms living in subterranean environments.

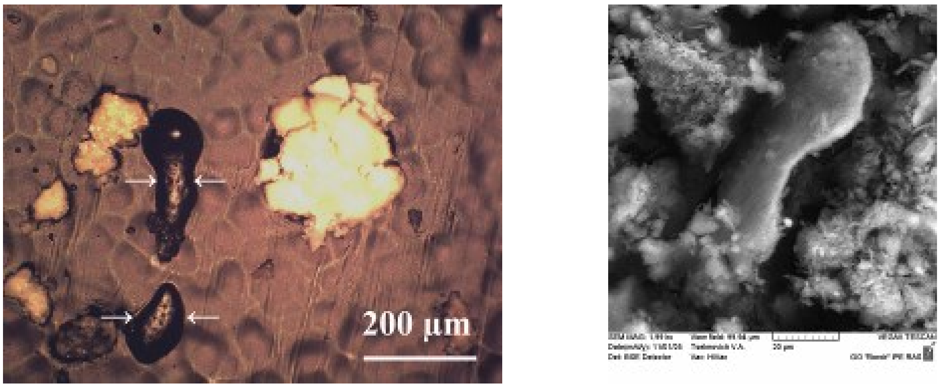
The discovery of cosmic dust in sedimentary rocks of caves in the Caucasus is of a great scientific significance. Cosmic dust consists of small particles (Fig. 5a, b, c) originating from outer space, including micrometeorites and fragments of comets (Tselmovich et al., 2025) and asteroids (Sungatullin et al., 2017). These particles constantly settle on the Earth's surface, although their concentration is extremely low. The very discovery of such particles demonstrates the high sensitivity of the chosen method of magnetic sample preparation and microscopic diagnostics.

The discovery of a magnetic anomaly in samples No. 14 and No. 15 indicates the presence of a cultural layer associated with foundry production. Variations in Irs, reflecting magnetite content in the soil (Fig. 2, samples 3, 5, and 9), may indicate a period of intensive vegetation growth and increased microbiological processes, accompanied by increased humidity and precipitation. Conversely, a decrease in magnetite content may indicate droughts and reduced productivity of terrestrial ecosystems (Fig. 2, samples 4, 6, 8, 12, and 13).



a) b)

Fig. 3. Particles with iron films: a) Sample 1, b) Sample 12

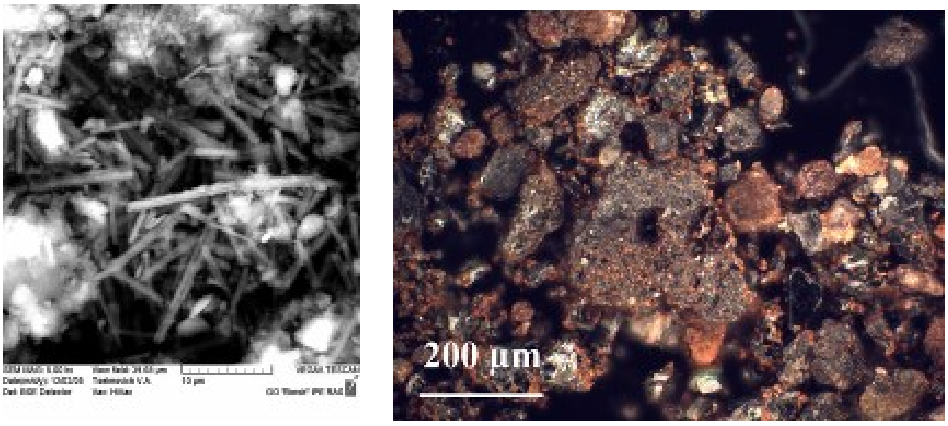


a) b)

Fig. 4. Sample 2: Volcanic dust particles, fused magnetites: a) optical, b) SEM.

a) b) c)

Fig. 5. Particles of background cosmic dust and cometary material: a) magnetite microsphere; b) strip of flaky Fe; c) particle of presumably cometary origin.



a) b)

Fig. 6. a) hematite needles; b) particles of technogenic magnetite (foundry traces).

Conclusions. Studying the composition of magnetic minerals provides important clues regarding climate change and processes that occurred in different historical eras. Their study allows us to reconstruct a picture of ancient geological processes and climate change, which is of great importance for understanding the current state of the region's ecosystems. Magnetic minerals serve as a reliable source of information about the past and present of the Caucasus's natural features, facilitating the development of scientific research and the preservation of the region's natural heritage. During the study of magnetic minerals from sedimentary deposits in Kuvinskaya Cave, magnetite particles of volcanic origin were discovered in lithological layer 5 (sample no. 2), providing insight into the scale and frequency of volcanic eruptions. Variations in magnetite content may indicate increased humidity when the content increases, while decreased levels may indicate droughts and reduced productivity of terrestrial ecosystems.

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References:

1. Golovanova L.V., Doronichev V.B., Doronicheva E.V. Kuvinskaya Cave, Layer 5 // Climate Dynamics and Adaptation Models in the Middle and Upper Paleolithic of the Northwestern Caucasus. -2022. -P. 205-209.
2. Pospelova G.A., Golovanova L.V., Doronichev V.B., Tselmovich V.A. Magnetic and Mineralogical Characteristics of Rocks from the Paleolithic Site in Mezmayskaya Cave (North Caucasus) // Physics of the Earth. - 2011. - No. 7. -P. 86-96.
3. Sungatullin R.Kh., Sungatullina G.M., Zakirov M.I., Tselmovich V.A., et al. Microspheres of Cosmic Origin in Carboniferous Deposits of the Usolka Open-Cut, Cis-Ural Depression. Geology and Geophysics. -2017. -No. 1.- P. 74–85.
4. Tselmovich V.A., Shelmin V.G., Maxe L.P. Microscopic Traces of the Chulym Bolide, 1984 Fall // Lithosphere. – 2025. - Vol. 25.- No. 4.- P. 961–976. DOI
5. Djerrab A., Aïfa T. Contribution of Rock Magnetism to Stratigraphy and Palaeoenvironment of the Karaïn Cave Infill, Antalya, Turkey // Stud Geoph Geod. - 2010. -54. - P.49–76. https://doi.org/10.1007/s11200-010-0003-0
6. Pospelova G.A., Król E., Levkovskaya G.M. et al. Magnetic, paleomagnetic and palynologic studies of Paleolithic deposits of the Akhshtyrskaya cave (Russia) // Acta Geophys. -2007. -55. -P 619–639. https://doi.org/10.2478/s11600-007-0019-1

Tselmovich V.A., Aphinogenova N.A. Use of heterophase oxidized titanomagnetites in the diagnosis of paleomagnetic data. *UDC 550.383.3:549.641.23*

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Annotation. The use of heterophasically oxidized titanomagnetites (HPO TM), as the most common carriers of rock magnetization, in the diagnosis of the suitability of samples for paleomagnetic studies has significantly expanded the possibilities of paleomagnetism, allowing us to gain a deeper understanding of the evolution of the Earth's magnetic field and related processes. Further developments in data processing and interpretation techniques promise to open up new horizons in the study of the deep mechanisms of the Earth's functioning. Oxidation of titanomagnetite stabilizes its magnetic properties, making them less sensitive to subsequent changes in temperature and pressure. This is important for maintaining the primary magnetization of the rock, which reflects the state of the Earth's magnetic field at the time of rock formation. Specific cases of successful application of detailed microscopic studies of HPO TM in

paleomagnetic studies of Proterozoic samples can also be used for new objects. The use of electron microscopy and X-ray diffractometry to visualize the phase distribution and identify microstructural features, combined with magnetic data, made it possible to create a set of features for selecting samples suitable for paleomagnetic studies.

***Keywords**: titanomagnetites; heterophase oxidized grains; rock magnetization carriers; proterozoic; microscopy; microstructure; X-ray diffractometry; paleomagnetic studies*

Introduction. Evaluating the validity of paleomagnetic data is an important task in geology. It helps determine the reliability of the results obtained and eliminate the influence of factors that distort the original orientation of rocks. One of the key aspects of this evaluation is the microstructural study of magnetic grains contained in the rock. The microstructure of magnetic grains includes crystal morphology, phase distribution, lattice defects, and grain boundaries. These characteristics depend on the conditions of rock formation, the type of magnetism, and subsequent metamorphic or weathering processes. The main types of microstructure include: 1. Simple single crystals: homogeneous grains that retain the primary magnetic structure. 2. Aggregates of small particles: consist of many submicron grains combined into clusters. 3. Zonal structures: characterized by variations in composition and structure along the grain radius. 4. Composition of magnetic grains. The chemical composition of magnetic grains also plays an important role in the interpretation of paleomagnetic data. The most common minerals possessing remanent magnetization are magnetite (Fe_3O_4), hematite (Fe_2O_3) and titanomagnetites (TM). Their ratio and oxidation state influence the stability of the magnetization vector. Microscopic observations of magnetic particles are used for paleomagnetic interpretations—the study of the natural remanent magnetization of rocks. The goal is to determine the composition of magnetic minerals and elucidate the nature of the magnetization, which is important for dating geological complexes, their age correlation, and reconstructing the positions of continents, continental blocks, and lithospheric plates. Remanent magnetization persists in rocks even after the external magnetic field ceases, and its vector coincides with the orientation of the Earth's magnetic field at the time of mineral formation.

Subject and Methods of Study. The subject of study is titanomagnetites. These minerals are of particular interest for paleomagnetic studies, which allow us to reconstruct the positions of continents and past tectonic processes.

What is TM HPO? TM is a complex oxide mineral, a solid solution of magnetite $(1\text{-}x)\cdot Fe_3O_4$ and ulvospinel $x\cdot Fe_2TiO_4$. Its crystal structure varies depending on the titanium content, which affects its magnetic properties. When TM undergoes oxidation, phases with different oxygen contents form, leading to the formation of heterophase structures. These structures are characterized by the presence of regions with different magnetic properties, making them valuable objects for studying paleomagnetic phenomena.

HPO TM minerals that have undergone partial oxidation, resulting in the formation of mixed phases of magnetite and hematite, are often used. These minerals have specific magnetic properties that depend on the degree of oxidation and grain size. They are important for paleomagnetic studies because they are able to retain the remanent magnetization acquired during rock formation. This magnetization reflects the direction and intensity of the Earth's ancient magnetic field, allowing us to determine the region's geographic location in the past, including the Proterozoic Era. The Proterozoic Era spans the period from approximately 2.5 billion to 538.8 million years ago. This time is characterized by significant changes in the Earth's crust, including the formation of supercontinents and major tectonic processes. Studying the magnetic properties of rocks from this period helps us understand global changes in the Earth's structure and the evolution of its magnetic field.

Types of Magnetic Phases in HPO TM. TM HPO is a complex system consisting of several types of magnetic phases. Each phase has its own unique physical and chemical properties, which significantly influences the magnetic characteristics of the mineral. The main types of magnetic phases in TM GFO are:

Maghemite (γ- Fe_2O_3). Formed by the partial oxidation of magnetite. This phase is characterized by a high Curie temperature (~675°C) and significant coercivity, making it an important component in preserving primary magnetic signals in rocks.

Hematite (α-Fe_2O_3). Formed by the complete oxidation of magnetite. It has a high Curie temperature (~680°C) and low remanent magnetization. Despite this, hematite plays a key role in the formation of secondary magnetic components in rocks.

Ultrafine magnetite (UFM). It occurs during the partial reduction of maghemite or hematite. Due to its small size, UFM exhibits superparamagnetic properties, which forms weak but stable magnetic components.

Titanomagnetite. Contains significant amounts of titanium, which substitutes for iron in the crystal lattice. This type of magnetite is characterized by a lower Curie temperature and increased oxidation resistance, which maintains primary magnetization even under prolonged exposure to atmospheric factors.

Titanium ferrites. Formed through complex oxidation reactions involving titanium substitution in the magnetite structure. These phases exhibit specific magnetic properties depending on the oxidation state and titanium concentration.

The Importance of Distinguishing Different Phases. Distinguishing these magnetic phases is critical for properly understanding paleomagnetic data. Each phase type makes a unique contribution to the overall magnetic pattern of a rock. For example:

Primary magnetic signals are often associated with preserved magnetite and TM phases. Secondary magnetic components are typically caused by the formation of hematite, maghemite, and sphene (titanite) during post-diagenetic processes.

Superparamagnetic effects observed due to the presence of ultradispersed magnetite influence the stability and intensity of magnetic records.

Microscopic observations of magnetic minerals are used in paleomagnetic interpretation to study the composition of magnetic minerals and elucidate the nature of the magnetization of rocks. This is necessary because natural remanent magnetization in rocks can consist of several components of different ages and directions, and these components can differ in the type of magnetization (orientational, thermoremanent, chemical, etc.) and the magnetic mineral that carries the magnetization. The combined use of microscopic studies with X-ray diffraction and magnetic methods allows for a detailed understanding of the carrier sets in specific objects. To diagnose the primary magnetization of magnetism carriers among HPO TM, it is important to consider a number of key characteristics of the microstructure and chemical composition of the minerals. These features allow us to determine the origin of the mineral's magnetic properties and establish the conditions under which primary magnetization formed.

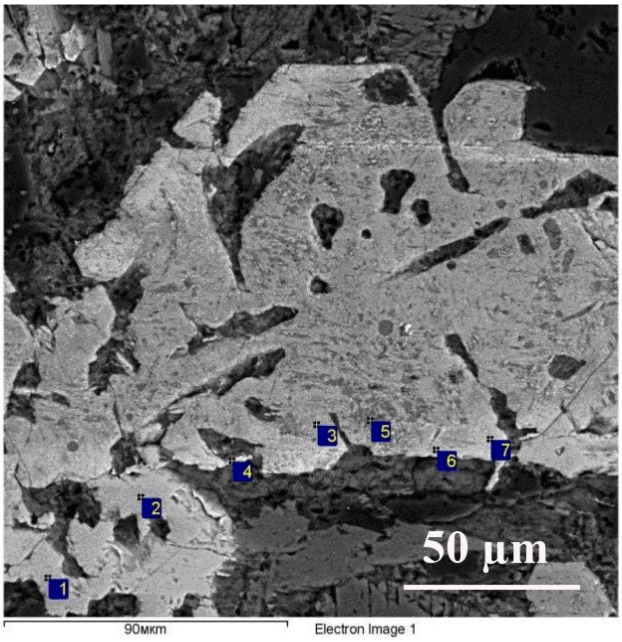
Microstructure. Microscopic examination reveals important structural features of titanomagnetites that influence their magnetization patterns: 1. Domain structure. The domain structure characterizes the distribution of spontaneous magnetization within the mineral-bearing grains. A regular and uniform domain structure indicates stable natural remanent magnetization (NRM). This is an important indicator for assessing the preservation of primary magnetization, since structural defects and disturbances may indicate secondary alterations. 2. Presence of inclusions and pores. The presence of small mineral inclusions (e.g., quartz, pyroxene, olivine) and pores affects NRM stability. Frequent inclusions contribute to the formation of weak magnetization zones and indicate a possible disruption of the original magnetization vector orientation. 3. Grain size. Large grains of titanomagnetite HPOs are more resistant to alteration and retain information about the primary NRM longer. 4. Surface oxidation. Changes in surface color and morphology indicate the degree of oxidation of TM. Oxidized areas often have reduced magnetization. 5. Chemical composition. Chemical composition also plays a key role in diagnosing the primary magnetization of TM: 5.1. Fe^{2+}/Fe^{3+} ratio. This ratio determines the degree of oxidation and magnetic properties of the material. A high Fe^{3+} content is associated with the formation of less magnetic forms, while the predominance of Fe^{2+} provides high magnetizability. 5.2. Presence of Ti, Mg, and Al. These elements affect the crystal structure and physicochemical characteristics of minerals. An increased amount of Ti and Al promotes the formation of weakly magnetized phases, such as ulvospinel and hercynite, worsening the preservation of the primary magnetization. 5.3. Trace Concentration. The presence of Mn, Ni, Cr, and Co traces can significantly alter magnetic properties and influence NRM formation. For example, high Mn and Ni contents increase NRM stability, while Cr reduces magnetic susceptibility. Thus, the identification and quantification of various magnetic phases in terrestrial magnetic fields are essential steps in paleomagnetic studies, enabling an accurate reconstruction of the Earth's magnetic field history.

Research (Tauxe, 2016; Shcherbakova et al., 2017; Shcherbakova et al., 2020; Shcherbakov et al., 2020; Shcherbakova et al., 2023) has shown that terrestrial magnetic fields are reliable indicators of ancient magnetic fields. They allow us to reconstruct the movement of continents and determine their past positions. Research shows that some regions, now widely separated, were part of a single continental massif during the Proterozoic.

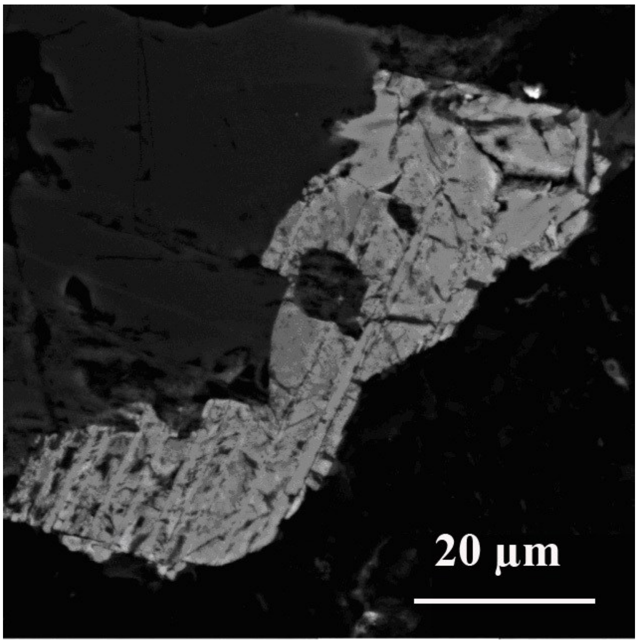
Advantages of HPO TM in paleomagnetic data analysis. HPO TM are unique mineral components that offer several advantages in paleomagnetic studies. Key advantages: 1. Resistance to environmental changes. One of the main advantages of HPO TM is their resistance to changing environmental conditions. The oxidation process stabilizes the magnetic properties of minerals, reducing their sensitivity to temperature and pressure fluctuations. This ensures the preservation of the primary magnetization of the rock, which reflects the state of the Earth's magnetic field at the time of its formation. 2. Diversity of magnetic properties. Heterophase structures of HPO TM are characterized by the presence of regions with different magnetic properties. This diversity allows for more accurate and detailed data on ancient magnetic fields. For example, differences in coercivity, remanent magnetization, and magnetic susceptibility provide a comprehensive approach to studying paleomagnetic records. Thus, the use of geomagnetic resonance (GPR) in paleomagnetic studies is an important tool for understanding the history of our planet and its tectonic activity.

Results. Discussion and Conclusions. Rejecting samples with signs of secondary alteration is crucial for obtaining reliable paleomagnetic information. The results of (Shcherbakova et al., 2023) are used as an example. Using a combination of microscopy and X-ray phase analysis, this rejection was performed on a collection of rocks aged ~1380 Ma, collected in the Udzha River valley within the Udzha aulacogen. Samples with minimal sphene content and characteristic HPO TM microstructure were selected for paleomagnetic determinations (Fig. 1). This resulted in a new, reliable determination of the geomagnetic field paleointensity Bdr, low in magnitude (4.54 μT) and corresponding to a low value of VDM ≈ 1.11 × 1022 Am^2.

Conclusions. Studying the microstructural features of TM allows us to identify the degree of influence of oxidation processes and other physicochemical transformations that significantly affect their ability to retain stable natural remanent magnetization. By assessing sample quality through a detailed study of its mineralogical nature, researchers are able to select the most suitable samples for high-precision paleomagnetic analyses. The accumulated experience is in demand when analyzing new objects and is being compiled into a database (microstructure atlas).



a)



b)

Fig. 1. Grains of HPO TM (a, b) with signs of sphenization.
a): (1, 2) ilmenite; (3, 4, 5) sphene + magnetite; (6, 7) sphene (low) + magnetite

Funding: his work was carried out under a state assignment from the Institute of Physics of the Earth, Russian Academy of Sciences.

References

Shcherbakov V. P. et al. On the reliability of absolute palaeointensity determinations on basaltic rocks bearing a thermochemical remanence //Journal of Geophysical Research: Solid Earth. – 2019. – Vol. 124. – №. 8. – P. 7616-7632. – https://doi.org/10.1029/2019JB017873.

Shcherbakova V. V. et al. An ultralow geomagnetic field intensity in the Mesoproterozoic based on studies of 1380 Ma old intrusive bodies from the Udzha aulacogen of the Siberian Platform //Izvestiya, Physics of the Solid Earth. – 2023. – Vol. 59. – №. 5. – P. 682-703. – https://doi.org/10.1134/S1069351323050105.

Shcherbakova V. V. et al. Paleointensity determination on Neoarchaean dikes within the Vodlozerskii terrane of the Karelian craton //Izvestiya, Physics of the Solid Earth. – 2017. – Vol. 53. – №. 5. – P. 714-732. – https://doi.org/10.1134/S1069351317050111.

Shcherbakova V. V. et al. Ultra-low palaeointensities from East European Craton, Ukraine support a globally anomalous palaeomagnetic field in the Ediacaran //Geophysical Journal International. – 2020. – Vol. 220. – №. 3. – P. 1928-1946. – https://doi.org/10.1093/gji/ggz566.

Tauxe L. Essentials of Paleomagnetism// Scripps Institution of Oceanography. – 2016. – 247 p. – ISBN/ASIN: 0520260317. – ISBN-13:9780520260313.

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Raman spectroscopy of synthetic Cu-bearing tourmaline. *UDC: 549.612;543.424.2*

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Abstract: Tourmaline-supergroup minerals are ring borosilicates that exhibit extensive isomorphism and exhibit piezoelectric and pyroelectric properties. Spectroscopic studies of this class of compounds contribute to a deeper understanding of their crystal-chemical features. In this study, Cu-bearing tourmaline was synthesized on a natural elbaite seed crystal by hydrothermal growth under thermogradient conditions at a temperature of 600/650 °C and a pressure of 150 MPa. The neon-blue overgrown layer, about 600 μm thick, shows a zonal distribution of elements, with copper reaching up to 15 wt.% CuO (~1.8 apfu). Raman spectra were collected from the zone of the overgrown layer with the highest copper content, over the range 150–4000 cm^{-1} in both $\bar{y}(zz)y$ and $\bar{y}(xx)y$ polarizations. A comparative analysis was then performed against the spectrum of the natural elbaite seed.

Keywords: *tourmaline; Raman-spectroscopy; hydrothermal synthesis; cuprum; crystal structure*

Introduction. Tourmalines constitute a diverse group of borosilicate minerals renowned for their structural complexity and broad chemical variability. Their general structural formula can be represented as $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, where $X = Na^+$, Ca^{2+}, K^+ □ (= vacancy); Y – octahedral position occupied by Fe^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Li^+, Fe^{3+}, and Cr^{3+} atoms; Z – distorted octahedra occupied by Al^{3+}, Fe^{3+}, Mg^{2+}, and Cr^{3+} cations; T – tetrahedral position, can be occupied by Si^{4+}, Al^{3+}, and B^{3+} atoms; $V = OH^{1-}$ and O^{2-} and $W = OH^{1-}$, F^{1-}, and O^{2-}(Henry et al. 2011). The most significant compositional variations occur at the *X, Y, Z, W,* and *V* sites, and the extensive isomorphic substitutions within the tourmaline structure give rise to numerous end-member compositions, rendering their crystallochemistry particularly challenging to fully characterize (Bosi et al. 2005).

Cu-bearing tourmaline (Paraiba), famous for its neon-blue colour, was first discovered in 1988 by G. D. Barbosa in the hills of Paraiba, Brazil. Today, deposits in Mozambique and Nigeria are also widely known (Dutrow B. L., 2024). Natural Cu-bearing tourmalines typically contain only up to 2 wt.% CuO, as the geological coexistence of sufficient boron and copper is rare. Synthetic tourmalines, however, can incorporate 7-14 wt.% CuO (Vereshchagin, O.S. 2013, Ertl A. et al. 2013), far exceeding natural levels. This suggests that Cu-bearing tourmaline could potentially exist as a separate mineral species (Vereshchagin O.S. (2015). The goal of this study was to synthesize high-copper tourmaline and examine its spectroscopic features.

Materials and methods. Synthesis experiments were carried out in a high-pressure apparatus with gas heating at T = 600–650°C and P = 150 MPa using a gold capsule with a volume of 3 ml. The experimental setup was as follows: quartz rods, corundum, and CuO reagent were placed in the lower part of the gold capsule, while an elbaite seed crystal was suspended on a gold wire in the upper part. A solution of H_3BO_3 + NaF was poured into the capsule according to the filling coefficient. The capsule was then sealed using an argon arc welder, and the resulting seal was checked in boiling water. The duration of the experiment was two weeks. The chemical composition of the samples was determined on polished carbon-sprayed surfaces using a Tescan Vega II XMU scanning microscope with an INCA Energy 450 energy dispersive spectrometer (EDS). Raman spectra were obtained on a Renishaw instrument (RM1000) equipped with a Leica microscope using a λ = 532nm solid state laser, spectra were recorded at 50x magnification for 100s, in the range 100-1500 cm^{-1}.

Results and discussion. As a result, an overgrowth of bright neon-blue Cu-bearing tourmaline was obtained on the seed crystal (Fig. 1a). In addition, the run products contained spontaneously crystallized Cu-bearing tourmaline crystals (Fig. 2a), quartz (Fig. 2b) and topaz (Fig. 2c) were also found. The overgrown layer reaches 600 μm thick and is characterised by zonal distribution of elements (Fig. 1b). The copper content in the newly formed layer decreases moving away from the elbaite seed boundary to the periphery (Table 1).

Raman spectroscopy offers a powerful means of probing both long-range and short-range bonding arrangements in crystalline materials, providing complementary information on the connectivity between different crystallographic sites.

Factor group analysis of tourmalines predicts 28 *Ag* and 49 *Eg* Raman-active modes. In this study, on unpolarised spectra in the range 100 – 3800 cm^{-1}, 15 vibrations for elbaite and 14-20 vibrations for Cu-tourmaline with different intensities were detected. The Raman spectra measured from the points of three compositions T1, T2, T3 (Table 1) of Cu-bearing tourmaline and elbaite seed (Tz) are presented in Fig. 3a. The wavenumbers of the observed bands (cm^{-1}) and their attribution to the corresponding types of vibrations according to previously published works (Gasharova et al, 1997; Watenphul et al, 2016; Spivak et al, 2021).

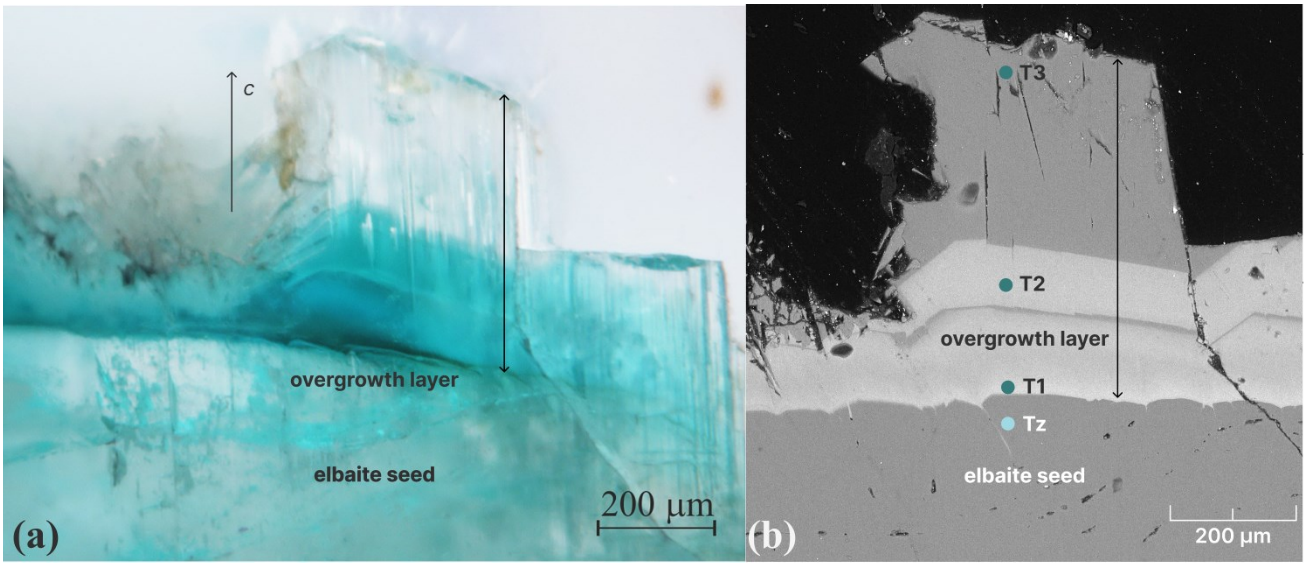

Fig. 1. (a) – an overgrown Cu-tourmaline layer formed on the surface of natural elbaite seed; (b) – SEM-image of zonal crystal of Cu-tourmaline layer

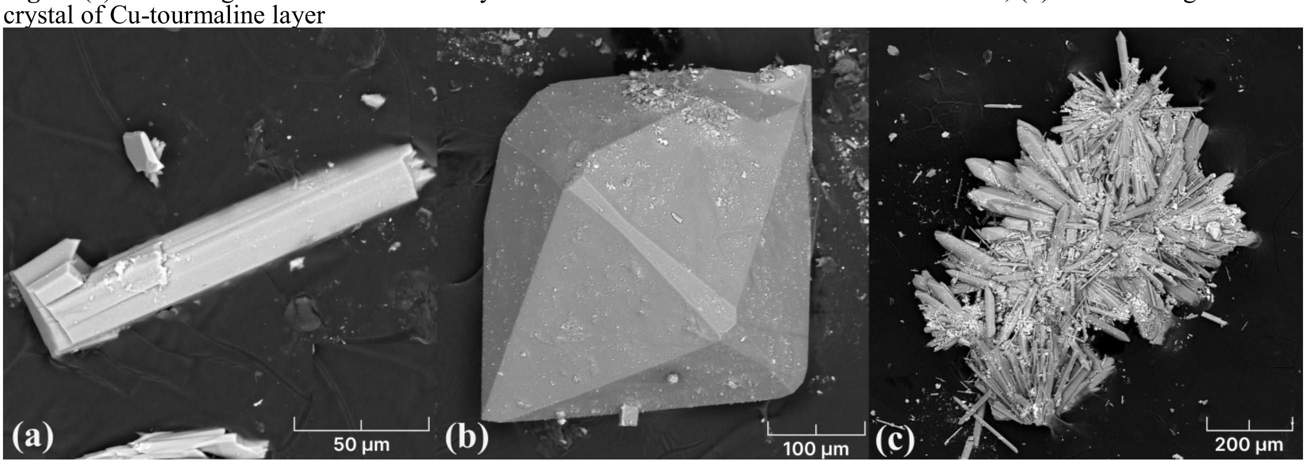

Fig. 2. SEM images of spontaneously crystallized Cu-bearing tourmaline crystals (a), and the associated phases of quartz (b) and topaz (c)

Table 1. Chemical composition of the seed crystal (Tz) and the overgrown layer of Cu-bearing tourmaline (T1-T3).

Component	Composition in wt%				*Apfu* on 15 cations *Y*+*Z*+*T*=15 Kt.			
	Tz	T1	T2	T3		T1	T2	T3
SiO_2	36.39	29.49	30.82	29.01	Si	5.25	5.59	5.01
Al_2O_3	40.95	36.76	36.34	48.88	Al	7.71	7.77	9.96
CuO	-	15.21	11.99	0.2	Cu	2.04	1.64	0.03
Na_2O	1.75	1.17	0.86	0.87	Na	0.40	0.30	0.29
CaO	0.76	-	-	-				
$B_2O_{3calc.}$	-	9.78	9.59	10.06	B	3	3	3
H_2O calc .	-	2.19	2.68	3.71	OH	4.00	3.75	2.72
Sum	**79.85**	**94.60**	**92.28**	**92.29**	**O**	**0.00**	**0.25**	**1.28**

In the range of 150-1500 cm^{-1} there are distinguished regions with corresponding vibrations: <160 cm^{-1} – vibrations of atoms in the *X*-site (Spivak et al, 2021), 160-280 cm^{-1} – vibrations associated with YO_6 octahedra (Gasharova et al, 1997; Watenphul et al), 280-460 cm^{-1} – vibrations associated with ZO_6 octahedra (Gasharova et al, 1997; Watenphul et al), 460-670 cm^{-1} – oxygen vibrations in Si_6O_{18} rings (Spivak et al, 2021), 670-750 cm^{-1} – vibrations associated with BO_3 groupings (Gasharova et al, 1997), 750-840 cm^{-1} – vibrations of B-O-Al bonds (Gasharova et al, 1997), 840-1100 cm^{-1} – internal vibrations of SiO_4 tetrahedra (Watenphul et al, 2016) (Fig. 2).

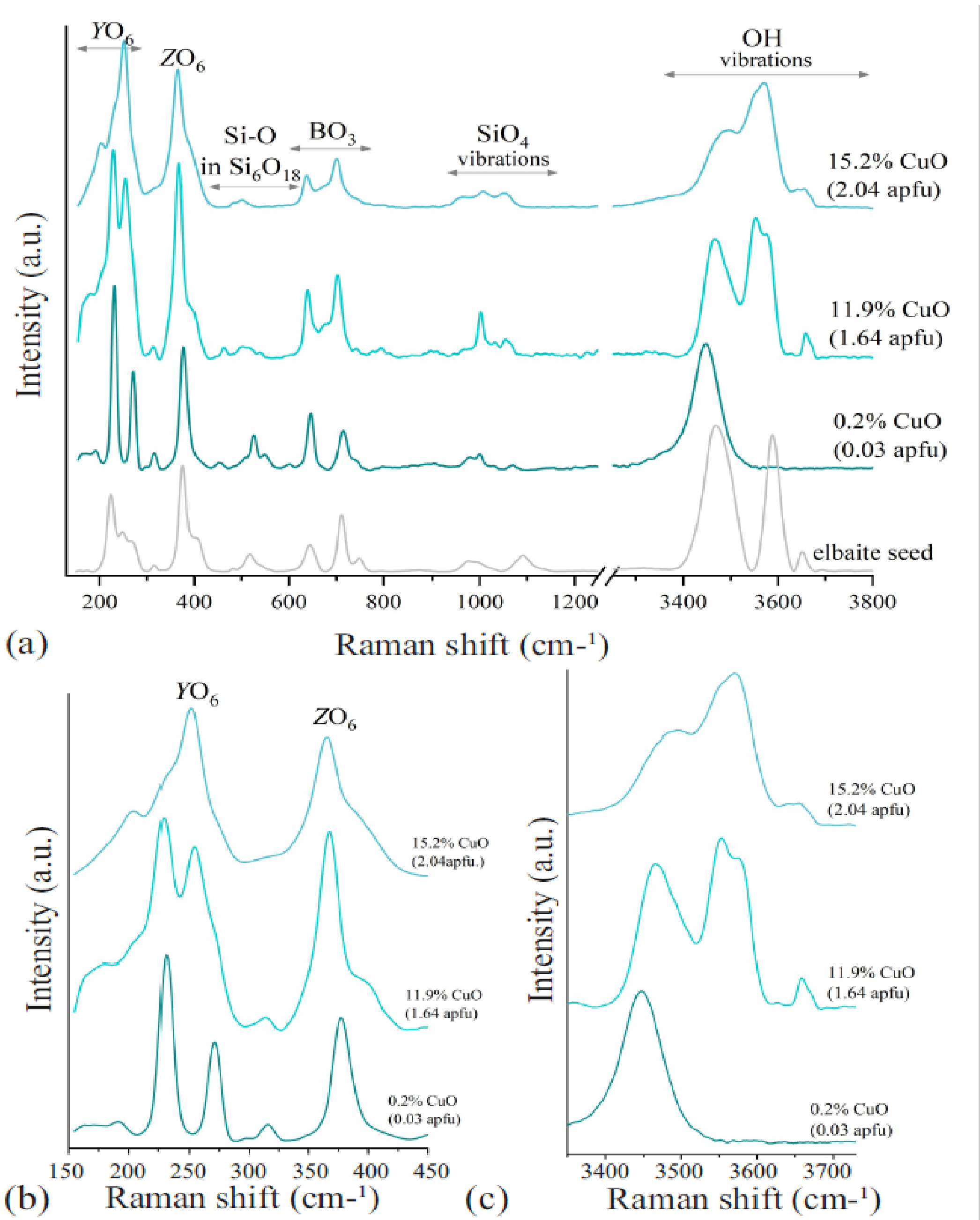

Fig. 3. Unpolarized Raman spectra of elbaite seed and Cu-bearing tourmaline with deferent Cu content (a), spectra in range 150-450 correspond to *Y*O_6 and *Z*O_6 octahedral vibrations (b) and 3400-3700 correspond the OH stretching region (c).

With increasing in Cu content, the Raman spectra exhibit a gradual evolution in bands' shape while showing only minor changes in peak positions. The most pronounced spectral modifications occur in the low-wavenumber region assigned to the *Y*O_6 and *Z*O_6 octahedral vibrations (Fig. 3b), as well as in the OH stretching region (Fig. 3c). Cu-rich zone is characterized by progressive band broadening, increased overlap between adjacent vibrational modes. In contrast, the bands associated with SiO_4 tetrahedra and BO_3 groups are comparatively less affected and do not display significant systematic frequency shifts.

In comparison with natural elbaite seed, two distinct bands merge into a single broad band in the *Y*O_6 octahedra vibration region for the Cu-bearing tourmaline. Moreover, a shoulder emerges and grows on the band in the *Z*O_6 octahedral vibration region as the Cu content increases. The elbaite seed exhibits two distinct OH bands at ~3460 and ~3585–3595 cm^{-1}. At 0.2 wt.% CuO, there is only one band at ~ 3447 cm^{-1}. At 11.9 wt.% CuO, the two-band pattern persists, but both bands broaden, overlap more, and become asymmetric. At 15.2 wt.% CuO, the spectrum no longer shows two distinct bands, instead, it consists of a broad asymmetric envelope with a prominent shoulder/hump and a band centered around ~3572cm^{-1}. An intense peak in the region from 950 to 1060 cm^{-1} is present both in the elbaite seed and in the accreted word and corresponds to the vibrations of Si-O bonds in SiO_4 tetrahedra.

Conclusion. As a result of the experiments, Cu-bearing tourmaline was successfully synthesized on a natural elbaite seed under thermogradient hydrothermal conditions at 600/650 °C and 150 MPa. The neon-blue overgrown layer, approximately 600 μm thick, displays a zonal distribution of copper with a maximum content of up to 15 wt.% CuO (~1.8 apfu). Raman spectroscopy revealed that the spectrum of the Cu-bearing layer is generally similar to that of the elbaite seed in the 150–1200 cm^{-1} range, but shows substantial changes in the OH-stretching region (3400–3800 cm^{-1}). With increasing Cu content, the originally two distinct OH bands gradually broaden, merge into a broad asymmetric envelope, and lose resolution, accompanied by the appearance and growth of a shoulder in the ZO_6 octahedral vibration region. The observed spectroscopic changes are attributed to the incorporation of Cu^{2+} into the *Y* and *Z* octahedral sites of the tourmaline structure, which perturbs the local environment of the OH groups and increases the diversity of their bonding configurations.

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References

1 Bosi F. Andreozzi G. B., Federico M., Graziani G., Lucchesi S. Crystal chemistry of the elbaite-schorl series // American Mineralogist. 2005. V. 90. №. 11-12. P. 1784-1792. https://doi.org/10.2138/am.2005.1827

2 Dutrow B. L., McMillan N. J., Henry D. J. A multivariate statistical approach for mineral geographic provenance determination using laser-induced breakdown spectroscopy and electron microprobe chemical data: A case study of copper-bearing tourmalines //American Mineralogist. – 2024. – T. 109. – №. 6. – C. 1085-1095 https://doi.org/10.2138/am-2023-9164

3 Ertl A. et al. Structural and chemical investigation of a zoned synthetic Cu-rich tourmaline //Mitteilungen der Österreichischen Mineralogischen Gesellschaft. – 2013. – T. 159. – C. 53.

4 Gasharova B., Mihailova B., Konstantinov L. Raman spectra of various types of tourmaline // European Journal of Mineralogy. 1997. V. 9. №. 5. P. 935-940. https://doi.org/10.1127/ejm/9/5/0935.

5 Henry, D. J., Novak, M., Hawthorne, F. C., Ertl, A., Dutrow, B. L., Uher, P., & Pezzotta, F. Nomenclature of the tourmaline-supergroup minerals // American Mineralogist. 2011. V. 96. №. 5-6. P. 895-913. https://doi.org/10.2138/am.2011.3636

6 London D. Experimental synthesis and stability of tourmaline: a historical overview // The Canadian Mineralogist. 2011. V. 49. №. 1. p. 117-136. https://doi.org/10.3749/canmin.49.1.117

7 Rozhdestvenskaya I.V., Setkova T.V., Vereshchagin O.S., Shtukenberg A.G., Shapovalov Yu.B. Refinement of Crystal Structures of Synthetic Nickel- and Cobalt-Containing Tourmalines // Kristallografiya. 2012. Vol. 57, No. 1, p. 63.

8 Setkova T., Balitsky V., Shapovalov Y. Experimental study of the stability and synthesis of the tourmaline supergroup minerals // Geochemistry International. 2019. V. 57. №. 10. P. 1082-1094. https://doi.org/10.31857/s0016-752564101064-1078

9 Setkova T., Borovikova, E., Spivak, A., Balitsky, V. Crystal growth and Raman spectroscopy of Ga, Ge-rich tourmaline. // Grafica editoriale. 2021. P. 97.

10 Setkova T.V., Shapovalov Yu.B., Balitsky V.S. // Doklady RAN. 2009. Vol. 424, No. 1, p. 94.

11 Spivak A., Borovikova E., Setkova T. Raman spectroscopy and high pressure study of synthetic Ga, Ge-rich tourmaline // Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2021. V. 248. P. 119171. https://doi.org/10.1016/j.saa.2020.119171

12 Vereshchagin O., Wunder B., Britvin S., Frank-Kamenetskaya O., Wilke F.D.H., Vlasenko N., Shilovskikh V. Synthesis and crystal structure of Pb-dominant tourmaline // American Mineralogist. 2020. V. 105. №. 10. P. 1589-1592. https://doi.org/10.2138/am-2020-7457

13 Vereshchagin O., Britvin S, Wunder B., Frank-Kamenetskaya O., Wilke F.D.H., Vlasenko N., Shilovskikh V., Bocharov V., Danilov D. Ln^{3+} (Ln^{3+} = La, Nd, Eu, Yb) incorporation in synthetic tourmaline analogues: Towards tourmaline REE pattern explanation // Chemical Geology. 2021. V. 584. P. 120526 https://doi.org/10.1016/j.chemgeo.2021.120526

14 Vereshchagin, O.S., Frank-Kamenetskaya, O.V., Rozhdestvenskaya, I.V., Zolotarev, A.A. Crystal chemical features of Cr, Cu and Ni-bearing tourmalines. Acta Crystallographica. – 2013. - A69. – P. 444

15 Vereshchagin O.S. Crystal chemistry of natural and synthetic tourmalines containing 3d elements. PhD dissertation, St. Petersburg State University (in Russian) – 2015.

16 Voskresenskaya I.E., Sternberg L.A. Synthesis of Tourmaline in Chloride Media // Kristallografiya. 1973. Vol. 19, No. 4, pp. 888-890.

Watenphul A., Schlüter J., Bosi F., Skogby H., Malcherek T., Mihailova B. Influence of the octahedral cationic-site occupancies on the framework vibrations of Li-free tourmalines, with implications for estimating temperature and oxygen fugacity in host rocks // American Mineralogist. 2016. V. 101. №. 11. P. 2554-2563. https://doi.org/10.2138/am-2016-5820.